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Irradiation-induced improvement of crystalline quality of epitaxially grown Ag thin films on Si substrates

K. Takahiro,[a] S. Nagata, and S. Yamaguchi
Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

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We report the Rutherford backscattering spectroscopy/channeling studies of epitaxial grown Ag films on Si(100) substrates irradiated with fast ions ($^{12}C^{++}$, $^{19}F^{++}$, $^{28}Si^{++}$) in the energy range between 0.5 and 4 MeV at 200 and −150 °C. The quality of the Ag films is improved considerably by ion irradiation. Irradiation with 0.5 MeV ^{28}Si ions to $2\times10^{16}/cm^2$ at 200 °C, for example, reduces the channeling minimum yield from 55% to 6% at the Ag surface. The improvement of crystalline quality is brought about by a decrease in mosaic spread in the Ag film. Also, it is found that the higher the crystallinity, the more radiation-induced defects are produced. The mechanism involved in the irradiation-induced improvement is discussed. © *1996 American Institute of Physics.* [S0003-6951(96)04645-1]

Ion beam irradiation provides an active research field for the low-temperature processing, especially in semiconductor technology. The generation and migration of vacancies induced by ion irradiation make it possible to synthesize and modify materials at temperatures well below those required for thermally activated processes. Ion beam induced epitaxial crystallization (IBIEC)[1,2] of an amorphous silicon and ion bombardment enhanced grain growth (IBEGG)[3,4] are typical phenomena accompanied by the vacancy generation and migration. We propose here that ion beams can be applied to improve the crystalline quality of an epitaxially grown metallic thin film. It is known that thin film prepared by a vacuum evaporation is composed of slightly misoriented crystallites. In order to obtain a film of better quality elimination of the slightly misoriented crystallites is required. Ion beam irradiation would decrease the number of misoriented crystallites due to grain growth similar to IBEGG, and improve the crystallinity of the films.

In this work, we investigate the irradiation-induced improvement of the crystalline quality of epitaxially grown Ag thin films evaporated on Si substrates. First, we demonstrate that irradiation of 0.5 MeV ^{28}Si ions at 200 °C improves the crystallinity of the Ag thin films. Then a variety of ion species, 2 MeV ^{12}C ions and 4 MeV ^{19}F ions as well as 0.5–2 MeV ^{28}Si ions, is used to irradiate the Ag/Si samples to examine the mechanism involved in the irradiation-induced improvement. In this case, the samples were irradiated at −150 °C.

Thin Ag films, 80 nm thick, were prepared using a conventional evaporation method in a vacuum system at a base pressure of 8×10^{-9} Torr or less. Single-crystal Si of [100] orientation was used as a substrate; this was rinsed in a dilute HF solution prior to the deposition. The deposition rate of the film was kept at 0.1–0.15 nm/sec. The Ag/Si sample was typically cut 10×15 mm^2. Some samples were annealed at 200 °C for 2 hours without irradiation. We shall refer to these annealed samples as ''non-irradiated samples.''

Irradiation with 0.5–2 MeV ^{28}Si ions, 4 MeV ^{19}F ions and 2 MeV ^{12}C ions was performed at the doses from 1×10^{16} to $2\times10^{16}/cm^2$ keeping the current density at 0.1 $\mu A/cm^2$ and 0.6 $\mu A/cm^2$ for low temperature (−150 °C) irradiation and elevated temperature (200 °C) irradiation, respectively, in order to avoid excess heating by irradiation. In this experiment, energies of the respective ions were chosen so that their projected ranges predicted by TRIM,[5] were much larger than the film thickness. Depth distribution of collision-induced defects is expected to be almost uniform under this condition.

Rutherford backscattering spectrometry (RBS) combined with the channeling technique with 1.3–4 MeV ^4He ions were carried out in order to characterize the samples before and after irradiation. The samples were mounted on a two axis goniometer, that allows both tilt and azimuthal rotation of the samples. Backscattered ions were detected with a SSD placed at an angle of 170°. The divergence of the analyzing beam was about 0.01°. All measurements were carried out at room temperature.

Figure 1 shows [100] aligned spectra taken from the samples before and after irradiation with 0.5 MeV ^{28}Si ions at 200 °C. The spectrum for the non-irradiated sample indi-

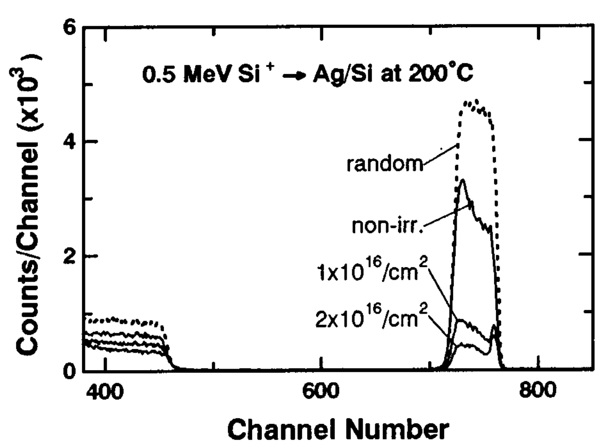

FIG. 1. Random (broken line) and [100] axial aligned (solid lines) spectra for 2 MeV ^4He ions incident on samples before and after 0.5 MeV $^{28}Si^+$ beam irradiation to doses of $1\times10^{16}/cm^2$ and $2\times10^{16}/cm^2$ at 200 °C.

[a]Electronic mail: takahiro@wani.imr.tohoku.ac.jp

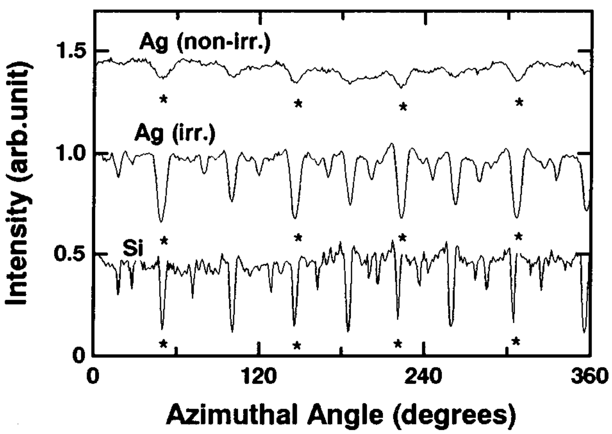

FIG. 2. RBS yields from Ag/Si as a function of an azimuthal angle for a tilt angle of 7°. ''Ag (non-irr.)'' and ''Ag (irr.)'' represent Ag yields from a non-irradiated sample and a sample irradiated to $2\times10^{16}/cm^2$ at 200 °C, respectively, and a yield of underlying Si (100) for the non-irradiated sample is indicated by ''Si.'' Four asterisks (*) in each curve correspond to {100} planes.

cates that the Ag thin film is grown epitaxially onto the Si(100) substrate. The epitaxial relationship can be studied by azimuthal angle scans of both the Ag and Si yields in RBS spectra as shown in Fig. 2. In Fig. 2, the planar dips are indexed referring to the minimum yields. Since the Ag film has a fourfold symmetry similar to the Si substrate, the epitaxial relationship between the Ag film and the Si substrate is determined to be Ag (100) ∥ Si (100) with Ag [011] ∥ Si [011].

As can be seen in Fig. 1, the minimum yield χ_{min} for [100] axial channeling is measured to be ~55% before irradiation, which is considerably large compared with a calculated value of 4% for a perfect Ag crystal for [100] orientation.[6] The χ_{min} value at the surface is decreased to approximately 6% by irradiation. This result shows that irradiation greatly improves the crystalline quality of the Ag thin film. The improvement of crystallinity of the Ag film can be seen also in Fig. 2.

Figure 3 represents [100] axial angular scans of Ag

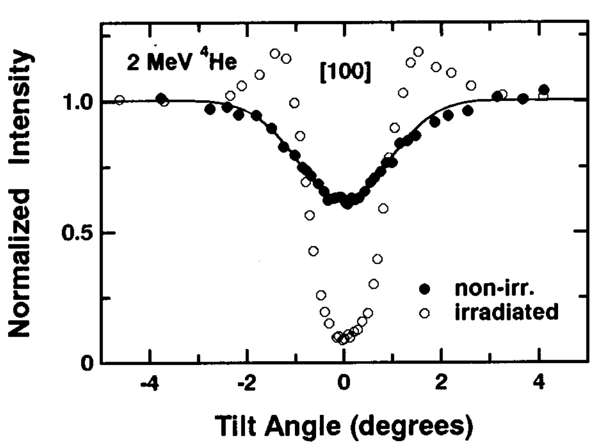

FIG. 3. Angular scans of normalized Ag yields along the [100] axis for 2 MeV ^{4}He ions incident on Ag/Si samples before (filled circles) and after (circles) irradiation of 0.5 MeV ^{28}Si ions to a dose of $2\times10^{16}/cm^2$ at 200 °C.

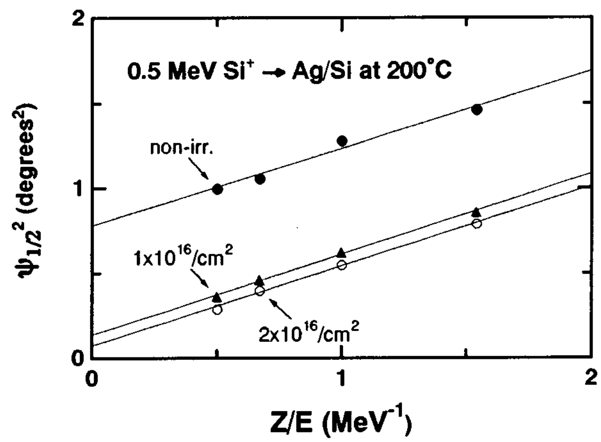

FIG. 4. A plot of squared half-width at half-maximum vs Z/E of the analyzing beam for a non-irradiated sample (filled circles), a low dose ($1\times10^{16}/cm^2$) sample (filled triangles) and a high dose ($2\times10^{16}/cm^2$) sample (open circles). Three lines are obtained by a least-square fitting method.

yields for the samples before and after irradiation with ^{28}Si ions to $2\times10^{16}/cm^2$ at 200 °C, where the yields are evaluated from the total area of the Ag peak in the RBS spectra. The channeling half angle $\psi_{1/2}$ as well as the χ_{min} are decreased considerably after irradiation. The presence of shoulders in the angular scan reflects good crystalline quality for the irradiated sample. As for the nonirradiated sample, the observed $\psi_{1/2}$ value of 1.13° is remarkably larger than the calculated value of 0.74° (Ref. 6) for a perfect Ag crystal. This discrepancy indicates that the non-irradiated film has a mosaic structure in which crystallites are slightly misoriented with each other, and therefore the decrease in $\psi_{1/2}$ by irradiation may be attributed to the reduction in the angular spread of crystallite orientations.

Next, we investigate the change in the angular spread of crystallite orientations in the Ag films before and after irradiation. The angular spread σ in the Ag film can be estimated by use of the method developed by Ishiwara and Furukawa.[7] Figure 4 shows the square of the observed $\psi_{1/2}$ values for the samples before and after irradiation as a function of Z/E (Z=2 in this work). According to the method of Ishiwara and Furukawa, intercepts of the vertical axis correspond to $\sigma^2\ln2$ values. From Fig. 4, we evaluate σ to be 1.1° for the non-irradiated sample, and to be 0.4° and 0.3° for the low dose ($1\times10^{16}/cm^2$) sample and the high dose ($2\times10^{16}/cm^2$) sample, respectively. The observed σ values are listed in Table I together with the χ_{min} values. Thus irradiation reduces the angular spread of crystallite orientations. It can be concluded, therefore, that the irradiation-induced

TABLE I. Observed χ_{min} and σ with respective to [100] orientation before and after irradiation of 0.5 MeV ^{28}Si ions at 200 °C. The χ_{min} values were measured at the Ag surface region just below the surface peak seen in Fig. 1. Calculated values for a perfect Ag crystal for 2 MeV ^{4}He ions are also presented for comparison.

Sample	χ_{min}(%)	σ (°)
Non-irradiated	55	1.1
$1\times10^{16}/cm^2$	12	0.4
$2\times10^{16}/cm^2$	6	0.3
Calculation	4	0.0

crystallinity improvement observed here is caused by the decrease in the angular spread around the [100] direction.

Finally, we shall discuss the mechanism involved in the crystallinity improvement induced by irradiation. The crystalline quality after ion irradiation up to $1\times10^{16}/\mathrm{cm}^2$ was examined by varying the ion energy and ion species at an irradiation temperature of $-150\,°\mathrm{C}$. Figure 5 shows the change in crystallinity α against the nuclear deposited energy for ion irradiation calculated by TRIM.[5] The α value is defined as $(\chi_{\text{non-irr.}}-\chi_{\text{irr.}})/\chi_{\text{irr.}}$, where $\chi_{\text{non-irr.}}$ and $\chi_{\text{irr.}}$ are minimum yields in aligned spectra for samples before and after irradiation, respectively. A positive value of α means improvement in the crystallinity. In Fig. 5, the larger deposition energy produces the better crystallinity. In other words, the better crystallinity is obtained as a higher concentration of defects is generated. This result implies that the collision-induced defects effectively decrease the mosaic spread of crystallite orientations in the Ag film. Furthermore, as can be seen in Fig. 5, we observed improvement in the crystallinity of the Ag film by each irradiation to $1\times10^{16}/\mathrm{cm}^2$ at $-150\,°\mathrm{C}$ for the all cases examined, although the Si substrates underlying the Ag films were heavily damaged or amorphized up to the Ag/Si interfaces. Thus collisional atomic rearrangements *not at the Ag/Si interface but in the Ag film* are responsible for the decrease in the spread of crystallite orientations. In addition, the difference in α between irradiation at 200 °C and -150 °C is found to be only $\sim$10%. This weak temperature dependence is similar to IBEGG.[1] From these results, the irradiation-induced improvement of crystallinity in the Ag film is supposed to be a special case of IBEGG. Major [100] oriented grains of larger size can grow through irradiation-induced annealing while minor smaller misoriented grains are diminished. As a result, we observed the decrease in the spread of crystallite orientations by irradiation. Additional methods like transmission electron microscopy observations may provide further information about the improvement of crystallinity induced by ion irradiation. Such experiments are now in progress.

In summary, we have demonstrated that ion irradiation improves the crystalline quality in Ag films grown on Si(100) substrates; the collision-induced defects reduce the angular spread of crystallite orientations in the film. Since the change in crystallinity depends on both defect concentration and temperature, the phenomenon observed is similar to irradiation enhanced grain growth. We suppose that major [100] oriented grains of larger size grow through the consumption of minor smaller misoriented grains by irradiation-induced annealing, which results in crystallinity improvement.

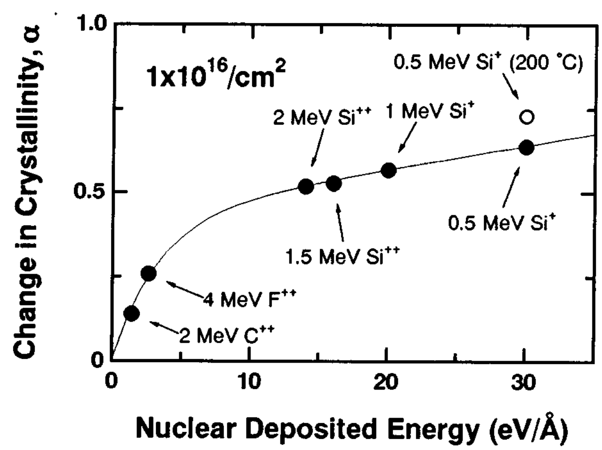

FIG. 5. The change in crystallinity α after irradiation to $1\times10^{16}/\mathrm{cm}^2$ at -150 °C (filled circles) and 200 °C (open circle) in one case, as a function of nuclear deposited energy at a depth of 40 nm for Ag film. The α value is defined as $(\chi_{\text{non-irr.}}-\chi_{\text{irr.}})/\chi_{\text{irr.}}$, where $\chi_{\text{non-irr.}}$ and $\chi_{\text{irr.}}$ are minimum yields in aligned spectra for samples before and after irradiation, respectively.

[1] H. A. Atwater, C. V. Thompson, and H. I. Smith, J. Appl. Phys. **64**, 2337 (1988).
[2] J. C. Liu, M. Nastai, and J. W. Mayer, J. Appl. Phys. **62**, 423 (1987).
[3] J. Nakata and K. Kajiyama, Appl. Phys. Lett. **40**, 686 (1982).
[4] I. Golecki, G. E. Chapman, S. S. Lau, B. Y. Tsaur, and J. W. Mayer, Phys. Lett. A **71**, 267 (1979).
[5] J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Ranges of Ions in Solids* (Pergamon, New York, 1985).
[6] J. S. Williams and R. G. Elliman, in *Ion Beams for Materials Analysis*, edited by J. R. Bird and J. S. Williams (Academic, Sydney, 1989), pp. 327–330.
[7] H. Ishiwara and S. Furukawa, J. Appl. Phys. **47**, 1686 (1976).